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The molybdenum isotopic composition of the modern ocean

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Natural variations in the isotopic composition of molybdenum (Mo) are showing increasing potential as a tool in geochemistry. Although the ocean is an important reservoir of Mo, data on the isotopic composition of Mo in seawater are scarce. We have recently developed a new method for the precise determination of Mo isotope ratios on the basis of preconcentration using a chelating resin and measurement by multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), which allows us to measure every stable Mo isotope (Nakagawa *et al*., 2008). In this study, 172 seawater samples obtained from 9 stations in the Pacific, Atlantic, and Southern Oceans were analyzed, giving global coverage and the first full depth-profiles. The average isotope composition in $\delta^{A/95}$Mo (relative to a Johnson Matthey Mo standard solution) was as follows: $\delta^{92/95}$Mo = –2.54 ± 0.16‰ (2SD), $\delta^{94/95}$Mo = –0.73 ± 0.19‰, $\delta^{96/95}$Mo = 0.85 ± 0.07‰, $\delta^{97/95}$Mo = 1.68 ± 0.08‰, $\delta^{98/95}$Mo = 2.48 ± 0.10‰, and $\delta^{100/95}$Mo = 4.07 ± 0.18‰. The δ values showed an excellent linear correlation with atomic mass of ^{A}Mo (R^2 = 0.999). Three-isotope plots for the Mo isotopes were fitted with straight lines whose slopes agreed with theoretical values for mass-dependent isotope fractionation. These results demonstrate that Mo isotopes are both uniformly distributed and follow a mass-dependent fractionation law in the modern oxic ocean. In addition, Mo isotopic analysis revealed that $\delta^{98/95}$Mo of the standard used in this study was 0.117 ± 0.009‰ lighter than the Mo standard that was used by Archer and Vance (2008). A common Mo standard is urgently required for the precise comparison of Mo isotopic compositions measured in different laboratories. On the other hand, our results strongly support the possibility of seawater as an international reference material for Mo isotopic composition.

Keywords: Mo isotopes, seawater, mass-dependent fractionation, reference material for Mo isotopic composition

INTRODUCTION

Molybdenum (Mo) has seven naturally occurring stable isotopes (^{92}Mo, ^{94}Mo, ^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo, and ^{100}Mo; de Laeter *et al*., 2003). Recent developments in analytical techniques, particularly the advent of multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), have allowed the precise determination of differences in the isotopic composition of Mo between samples and reference standards (Anbar *et al*., 2001; Siebert *et al*., 2001; Pietruszka *et al*., 2006; Nakagawa *et al*., 2008; Pearce *et al*., 2009). The reactivity of Mo in aqueous solution is very dependent on redox conditions and coexisting ligands, leading to significant variations in Mo isotopic composition as well as Mo concentrations in natural waters (Bertine, 1972; Helz *et al*., 1996; Zheng *et al*., 2000; Vorlicek and Helz, 2002; Helz *et al*., 2011; Wang *et al*., 2011). Mo isotopic data are generally reported in the literature in terms of $\delta^{98/95}$Mo or $\delta^{97/95}$Mo. The value of $\delta^{98/95}$Mo is defined by the following equation

$$\delta^{98/95}\text{Mo}(‰) = [(^{98}\text{Mo}/^{95}\text{Mo})_{\text{sample}}/(^{98}\text{Mo}/^{95}\text{Mo})_{\text{standard}} - 1] \times 1000 \quad (1)$$

and is converted to $\delta^{97/95}$Mo by multiplying 0.67 when the system follows mass-dependent fractionation. Though no commonly-used Mo isotopic standard currently exists (see later), the standards used by different laboratories do appear to be isotopically similar at the level of 0.1–0.2‰. Continental rock samples, such as granite, basalt, and clastic sediments, have $\delta^{98/95}$Mo of ~0.1‰ (Barling *et al*., 2001; Siebert *et al*., 2003). Ferromanganese oxides, which scavenge Mo from seawater in oxic conditions, have a light isotopic signature ($\delta^{98/95}$Mo = –1.0 to –0.5‰; (Barling *et al*., 2001; Siebert *et al*., 2003), whereas sediments formed in euxinic conditions (aqueous H_2S concentrations higher than ~11 μM, the action point pro-

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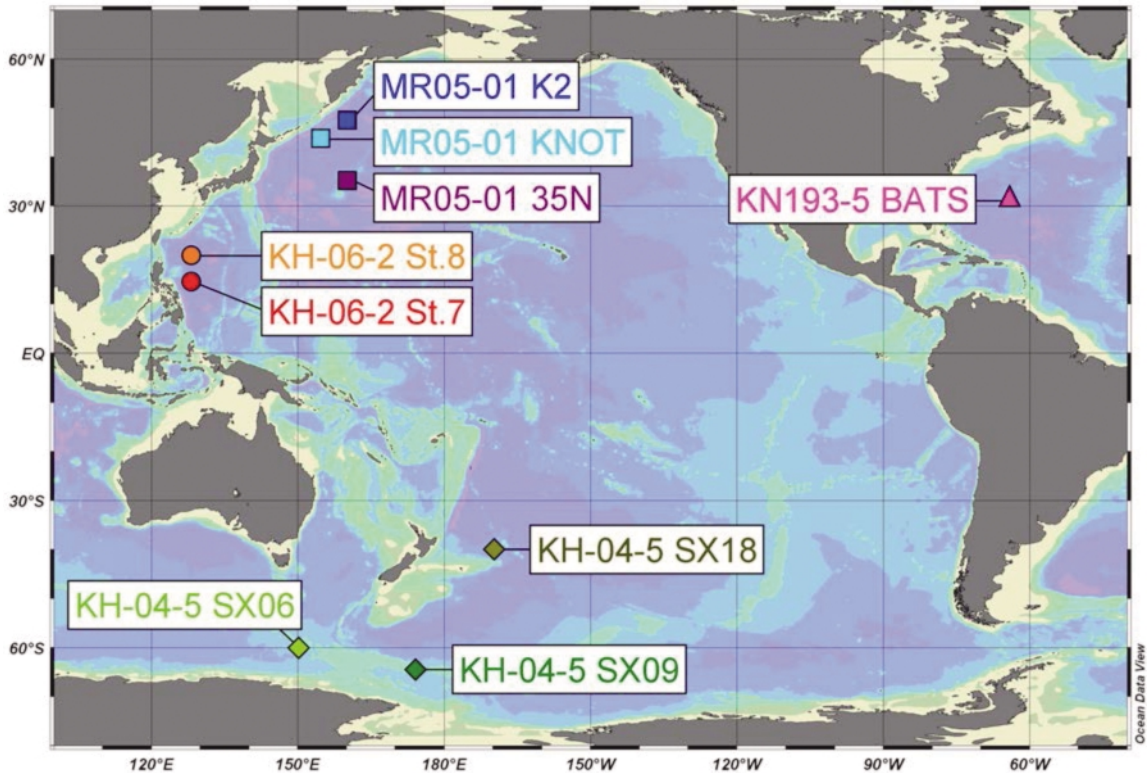

Fig. 1. Sampling locations. The map was prepared using Ocean Data View (Schlitzer, R., Ocean Data View, http://odv.awi.de, 2012).

posed by Helz *et al*. (1996) have a heavy isotopic signature ($\delta^{98/95}$Mo = 2.2 to 2.5‰; Barling *et al*., 2001; Arnold *et al*., 2004; Nägler *et al*., 2005; Neubert *et al*., 2008). Sediments formed beneath suboxic or anoxic bottom water (Poulson *et al*., 2006; Siebert *et al*., 2006; Poulson Brucker *et al*., 2009; Scheiderich *et al*., 2010) and carbonates (Voegelin *et al*., 2009) show variable isotopic compositions between the oxic and euxinic end-members. Besides these field observations, the isotopic fractionation of Mo has been experimentally evaluated for adsorption to manganese (Mn) oxides (Barling and Anbar, 2004; Wasylenki *et al*., 2008) and to iron (Fe) (oxyhydr)oxides (Goldberg *et al*., 2009), release from shales (Liermann *et al*., 2011), and assimilation by cyanobacteria (Zerkle *et al*., 2011). These results have indicated some potential for Mo isotopes in sediments to be a unique and powerful proxy in geochemical studies of past oceanic euxinia (Barling *et al*., 2001; Siebert *et al*., 2003; Archer and Vance, 2008; Poulson Brucker *et al*., 2009; Pearce *et al*., 2010b; Kendall *et al*., 2011), the rise of oxygen on the early Earth (Arnold *et al*., 2004; Siebert *et al*., 2005; Wille *et al*., 2007; Duan *et al*., 2010; Voegelin *et al*., 2010), and ocean circulation (Wen *et al*., 2011).

For accurate interpretation of geological Mo isotopic data, it is crucial to understand the cycle of Mo isotopes in the modern hydrosphere. Although pioneering studies assumed that the Mo input from rivers to the ocean would have a Mo isotopic composition similar to continental rocks ($\delta^{98/95}$Mo ~ 0‰; Siebert *et al*., 2003), recent studies on river and estuarine water revealed great variations in the isotopic composition of dissolved Mo ($\delta^{98/95}$Mo = –0.1 to 2.3‰; Archer and Vance, 2008; Pearce *et al*., 2010a; Scheiderich *et al*., 2010; Neubert *et al*., 2011). Data on the hydrothermal input are scarce. Low-temperature ridge-flank hydrothermal input is assumed to have an end-member value of $\delta^{98/95}$Mo ~ 0.8‰ based on observations at the Juan de Fuca Ridge (McManus *et al*., 2002), whereas an extremely light Mo ($\delta^{98/95}$Mo ~ –3.4‰) has been found in hydrothermal waters from Iceland (Pearce *et al*., 2010a).

Mo isotopic data for seawater are also scarce. Mo is present in oxic seawater predominantly as dissolved MoO_4^{2-} (Bertine, 1972). Mo has a concentration as high as 107 nmol/kg (normalized to a salinity (*S*) of 35) and is distributed uniformly in the modern oxic ocean with a residence time of ~800 ky (Collier, 1985; Sohrin *et al*., 1987; Tuit and Ravizza, 2003; Firdaus *et al*., 2008). Because of this uniformity, it has been implicitly assumed that Mo isotopes are homogeneously distributed in the ocean, with $\delta^{98/95}$Mo of ~2.3‰ on the basis of measure-

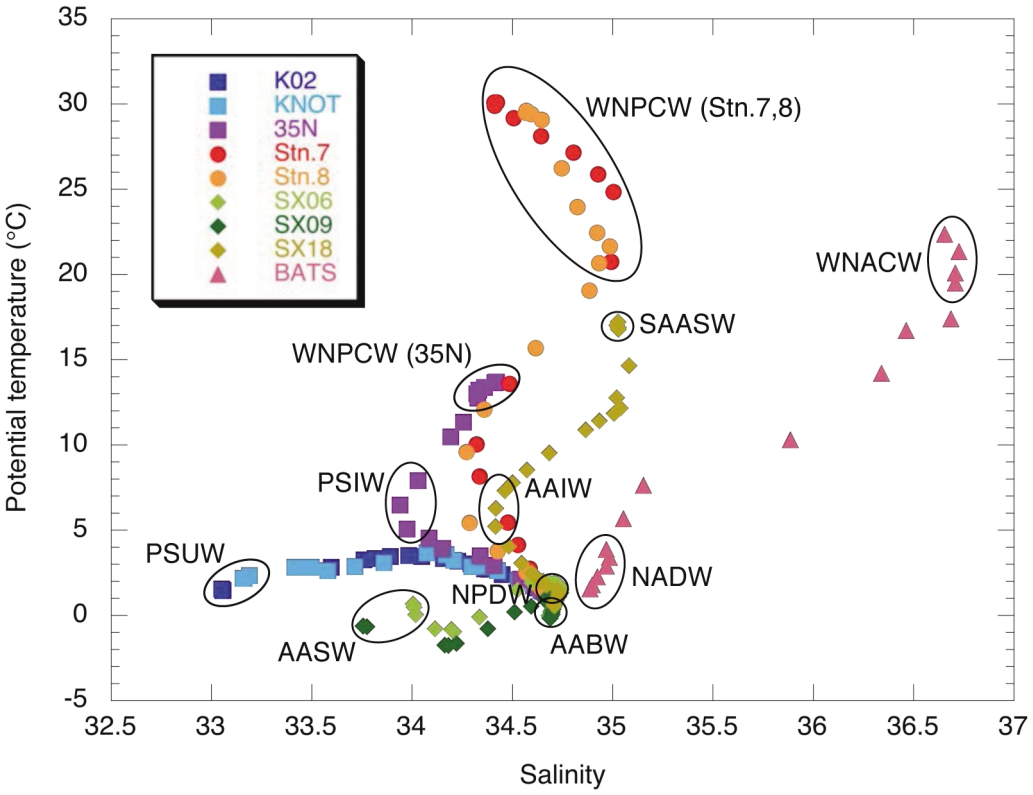

Fig. 2. T-S diagram. Identified water masses and the number of seawater samples are as follows: Pacific Subarctic Upper Water (PSUW, n = 11); Pacific Subarctic Intermediate Water (PSIW, n = 3); Western North Pacific Central Water (WNPCW; 35N; n = 7); WNPCW (Stn. 7, 8; n = 17); North Pacific Deep Water (NPDW, n = 25); Antarctic Surface Water (AASW, n = 6); Subantarctic Surface Water (SAASW, n = 4); Antarctic Intermediate Water (AAIW, n = 2); Antarctic Bottom Water (AABW, n = 4); Western North Atlantic Central Water (WNACW, n = 4); North Atlantic Deep Water (NADW, n = 6).

ment of a small number of samples (Barling *et al*., 2001; Siebert *et al*., 2003; Arnold *et al*., 2004; Archer and Vance, 2008). There has been no internationally-certified Mo isotope standard, and each of the above few data were reported relative to different working laboratory standards. In addition, a limited number of Mo isotopes were measured, because most studies employed mass bias correction techniques using elemental doping with zirconium (Zr), which interferes ^{92}Mo, ^{94}Mo, and ^{96}Mo, or using a double-spike made up of ^{97}Mo and ^{100}Mo (and the double spike approach assumes mass-dependent fractionation).

We have developed a new analytical method for determining the isotopic composition of dissolved Mo in seawater by employing a chelating resin technique for the preconcentration of Mo and an elemental doping technique using strontium (Sr) for mass bias correction (Nakagawa *et al*., 2008). This method is simple and rapid enough to allow the processing of a large number of seawater samples. In addition, we can measure every stable Mo isotope with this method. In the previous study (Nakagawa *et al*., 2008), we reported data on four kinds of seawater samples. In this study, we applied this technique to the isotopic analysis of dissolved Mo in 172 seawater samples obtained from the Pacific, Atlantic, and Southern Oceans. Thus we report for the first time on the global distribution of a full suite of the stable Mo isotopes in seawater. We also report nine full depth-profiles.

Materials and Methods

Seawater

Seawater samples were collected from nine stations (Fig. 1). Three stations (K2, KNOT, and 35N) in the western North Pacific were visited during the MR05-01 cruise of the R/V Mirai (JAMSTEC) in March 2005. Two stations (St. 7 and St. 8) in the Philippine Sea were visited during the KH-06-2 cruise of the R/V Hakuho Maru (JAMSTEC) in June 2006. Two stations (SX06 and SX09) in the Southern Ocean and SX18 in the western South Pacific were visited during the KH-04-5 cruise of the R/V Hakuho Maru from December 2004 to January 2005. Station BATS in the eastern North Atlantic was visited for US-GEOTRACES intercalibration activity during the

KN193-5 cruise of the R/V Knorr (Woods Hole Oceanographic Institution) in June 2008. The temperature-salinity (T-S) diagram for all the samples is shown in Fig. 2. Major water masses (Emery, 2001) are labeled on the diagram. Our samples contain seawater from at least ten major water masses in the modern ocean. Among these samples, the lowest dissolved oxygen concentration (of 15.9 μmol/kg) was found at 400 m depth at K02.

Onboard the R/V Mirai and Hakuho Maru, seawater samples from each depth were collected using Niskin-X sampling bottles (General Oceanics) that were mounted on a carousel sampler equipped with a CTD (Sohrin and Bruland, 2011). On deck, the seawater was transferred from the samplers into low-density-polyethylene (LDPE) bottles (Nalge Nunc Int.) using a silicon tube and filling bell (Nalge) to avoid contamination by airborne particles. The samples were immediately brought into a clean room laboratory (class 100), filtered through a 0.2-μm Nuclepore filter (Whatman) using a closed filtration system, acidified to pH ~ 2 using highly purified HCl, and stored at room temperature. On the R/V Knorr, seawater samples were collected using the US-GEOTRACES clean sampling system (Sohrin and Bruland, 2011). The sampling bottles were transferred to a clean sampling van, and the seawater samples were filtered through a 0.4-μm Nuclepore filter and acidified to pH ~ 2 using highly purified HCl.

Mo isotopic analysis

Details of our method are given in Nakagawa *et al*. (2008). Briefly, a 250-mL aliquot of seawater (pH ~ 2) was passed through a column (6 mm i.d., 30 mm bed height) of 8-hydroxyquinoline-immobilized hydrophilic vinyl polymer (TSK-8HQ) to collect Mo by forming a chelate. The adsorbed Mo was eluted with 60 mL of 2 M NH_3. The eluate was evaporated to dryness with a closed evaporation system, and the residue was dissolved in 5 mL of 0.05% ultrahigh-purity tetramethylammonium hydroxide (TAMAPURE-AA TMAH, Tama Chemicals). The resulting solution was used for the Mo isotopic ratio measurement by MC-ICP-MS (Nu Plasma 500, Nu Instruments), following doping with Sr to a concentration comparable with that of Mo (~500 ppb). The working Sr standard solution was prepared from NIST SRM 987 (Sr). The Sr isotope ratio used for correction was $^{86}Sr/^{88}Sr$, and a value of 0.1194 was assumed. The assumption of this particular value does not affect the calculation of relative isotope ratio differences between samples and standards. The Mo and Sr isotopic signals of the sample solution were measured in dynamic mode, with Mo and Sr isotopes alternatively integrated for 5 s and repeated for 40 cycles (20 cycles × 2 blocks). Mass discrimination of the Mo isotopes was externally corrected by normalizing to the Sr signals using an exponential law assuming a ratio of the betas of Sr and Mo of 1 (Nakagawa *et al*., 2008). To correct isotopic drifts of the instrument, a sample-standard bracketing technique was employed. The working Mo standard solution was prepared from a Johnson Matthey Specpure Mo plasma standard solution (Stock No. 38719, Lot No. 012773). Mo isotopic ratios of all the samples were expressed using δ-notation (e.g., $\delta^{98/95}$Mo in Eq. (1)) relative to the Johnson Matthey standard. The internal uncertainties (2SE) calculated from 40 cycles per measurement were typically ±0.09 and ±0.08 for $\delta^{98/95}$Mo and $\delta^{97/95}$Mo, respectively.

The Mo isotopic composition of the Johnson Matthey standard was precisely compared with the Mo ICPMS standard (CPI International) that was used by Archer and Vance (2008). The isotopic analyses were carried out at the University of Bristol, using a ThermoFinnigan Neptune instrument. Solutions were introduced into the mass spectrometer by means of a CPI PFA nebulizer and spray chamber fitted to a CETAC Aridus. Mass discrimination correction was achieved using a double spike technique.

Mo concentration determination

A small quantity of the preconcentrated sample solution was diluted and used for the determination of Mo concentrations, [Mo] (nmol/kg), by ICP-atomic emission spectrometry (ICP-AES, Optima 2000 DV, Perkin-Elmer). The calibration line was obtained with working standards prepared from a Mo standard solution (WAKO Pure Chemical Industries). The Mo recovery test from seawater verified quantitative recovery with RSD ~ 5% (Nakagawa *et al*., 2008).

RESULTS

Data for $\delta^{A/95}$Mo (A = 92, 94, 96, 97, 98 and 100) along with T, S and concentrations of oxygen and Mo are summarized in the Appendix table (available at http://www.terrapub.co.jp/journals/GJ/archives.html). There were a few outliers for both $\delta^{A/95}$Mo and [Mo]. Since they appeared to occur randomly because of mistakes in analysis, they were removed from the following analysis and discussion. We arbitrarily adopted a ±3SD cut-off, with the result that the rejected outliers made up less than 1.2% of the dataset.

The mean [Mo] was 106 ± 5 nmol/kg (2SD; n = 171). The normalized concentration to S = 35 was 107 ± 7 nmol/kg (n = 168). These values are in good agreement with literature data (Collier, 1985; Sohrin *et al*., 1987; Tuit and Ravizza, 2003; Firdaus *et al*., 2008). The results indicate that dissolved Mo in seawater was quantitatively collected by our technique.

The average isotope composition in $\delta^{A/95}$Mo was as follows: $\delta^{92/95}$Mo = –2.54 ± 0.16‰ (2SD; n = 170), $\delta^{94/95}$Mo = –0.73 ± 0.19‰ (n = 170), $\delta^{96/95}$Mo = 0.85 ± 0.07‰

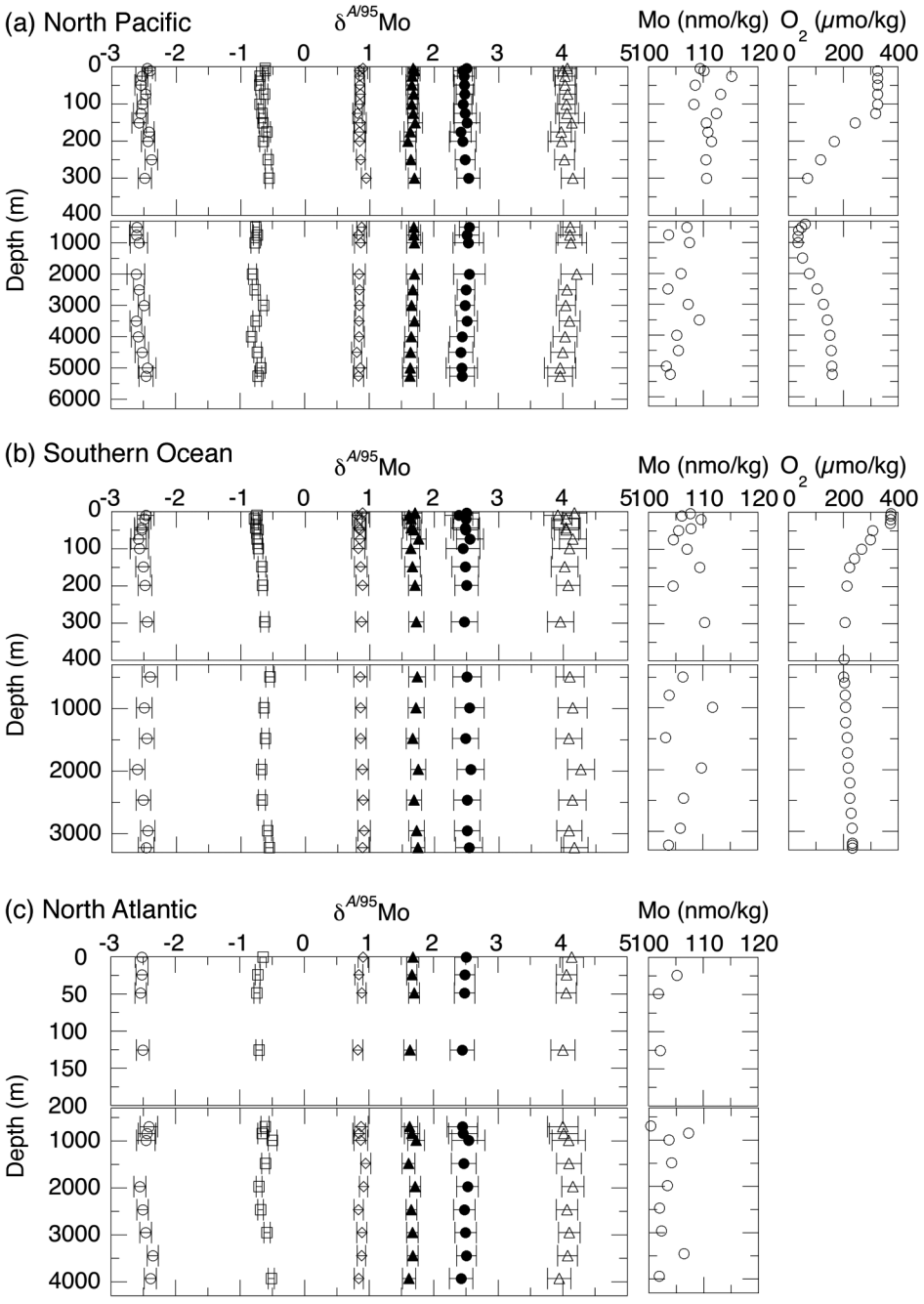

Fig. 3. Vertical profiles of the isotope composition and normalized concentration of dissolved Mo, as well as the oxygen concentration. For the isotope composition, open circles, $\delta^{92/95}$Mo; open squares, $\delta^{94/95}$Mo; open diamonds, $\delta^{96/95}$Mo; closed triangles, $\delta^{97/95}$Mo; closed circles, $\delta^{98/95}$Mo; open triangles, $\delta^{100/95}$Mo. Error bars indicate ±2SE of the integrations in each analysis. (a) KNOT in the North Pacific Ocean; (b) SX09 in the Southern Ocean; (c) BATS in the North Atlantic Ocean.

(n = 170), $\delta^{97/95}$Mo = 1.68 ± 0.08‰ (n = 171), $\delta^{98/95}$Mo = 2.48 ± 0.10‰ (n = 171), and $\delta^{100/95}$Mo = 4.07 ± 0.18‰ (n = 171). The relatively large SD for $\delta^{92/95}$Mo, $\delta^{94/95}$Mo and $\delta^{100/95}$Mo may be attributed to interference from seawater-derived ^{92}Zr, ^{94}Zr and ^{100}Ru, respectively. Vertical profiles of $\delta^{A/95}$Mo and the normalized concentration of Mo at three stations in the North Pacific, Southern, and North Atlantic Oceans are shown in Fig. 3. The profiles of oxygen are also shown for the stations in the North Pacific and Southern Oceans. Every $\delta^{A/95}$Mo

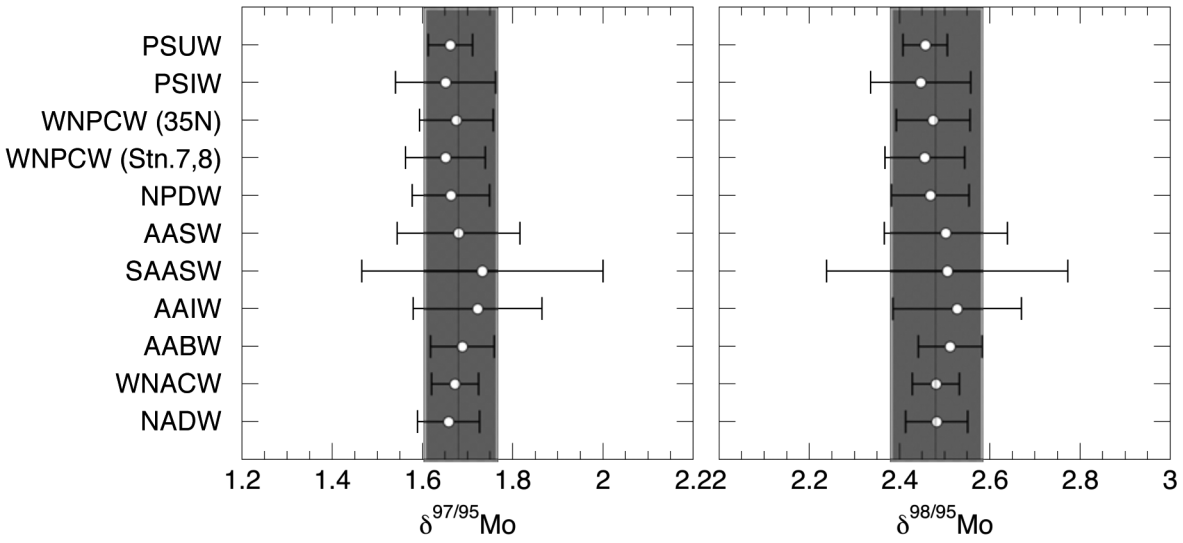

Fig. 4. $\delta^{97/95}$Mo and $\delta^{98/95}$Mo for each water mass. Open circles and error bars indicate the mean ±2SD for the multiple samples from each water mass. Overall mean ±2SD for all seawater samples ($\delta^{97/95}$Mo = 1.68 ± 0.08‰, $\delta^{98/95}$Mo = 2.48 ± 0.10‰) are shown as the vertical bars and grey shadings. The water mass abbreviations are given in Fig. 2.

showed uniform profiles at the other six stations as well as the above three stations. There are no significant inter ocean variations. The average and ±2SD of $\delta^{97/95}$Mo and $\delta^{98/95}$Mo for each water mass are plotted in Fig. 4. The SD was relatively large for some water masses, such as PSIW (n = 3), AASW (n = 6), SAASW (n = 4) and AAIW (n = 2). The reason is not clear at present. The averages for each water mass are within the range of the total average ± 2SD, suggesting that the formation of water mass does not cause significant mass fractionation among the Mo isotopes.

Redox state is a major factor controlling the fractionation of Mo isotopes, as summarized in the introduction. The values of $\delta^{A/95}$Mo are plotted against the oxygen concentration in Fig. 5. The oxygen concentration data were available for 146 samples from the Pacific and Southern Oceans. It is clear that there are no significant variations in $\delta^{A/95}$Mo as a function of the oxygen concentration. The results indicate that oxic fractionation is expected for Mo when the oxygen concentration is higher than 16 μmol/kg.

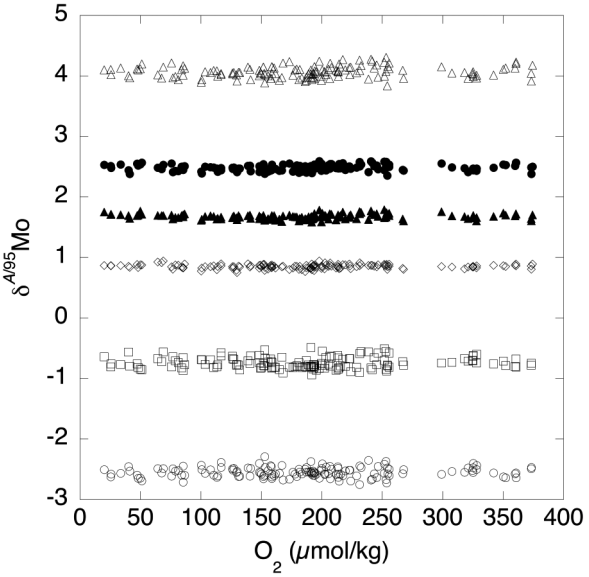

Fig. 5. Plot of $\delta^{A/95}$Mo against the oxygen concentration in the Pacific and Southern Oceans.

Discussion

Homogeneity of Mo isotopes in the modern oxic ocean

We did not observe significant deviations for either the Mo concentration or isotopic composition, within the precisions of our methods (5 nmol/kg for [Mo] and 0.10‰ for $\delta^{98/95}$Mo in 2SD). Poulson Brucker *et al*. (2009) proposed a revised modern marine Mo budget by utilizing Mo isotopic data. According to this model, the global Mo input to the ocean consists of a riverine flux of ~1.8×10^8 mol/y and a low-temperature hydrothermal flux of ~0.2 $\times 10^8$ mol/y. Three major sinks are proposed. The flux of Mo into oxic Mn-rich sediments is estimated to be ~0.9×10^8 mol/y. The continental margin sink, underling waters that are depleted in free oxygen but with sulfide concentrations below the action point of ~11 μM, has a flux of

~0.9×10^8 mol/y. The euxinic sink flux is estimated to be ~0.1×10^8 mol/y. Typically, the Mo concentration is conservative against *S* in estuaries and continental shelves (Head and Burton, 1970; Sohrin *et al*., 1999). $\delta^{98/95}$Mo is also more-or-less conservative in the two estuaries that have been studied—i.e., $\delta^{98/95}$Mo shows a linear correlation with a reciprocal of Mo concentration 1/[Mo] (Archer and Vance, 2008; Pearce *et al*., 2010a). A discharge-weighted global riverine average input flux was estimated to have [Mo] = 6 nmol/kg and $\delta^{98/95}$Mo = 0.7‰ (Archer and Vance, 2008). The modern seawater average of *S* = 35 is estimated to have [Mo] = 107 nmol/kg and $\delta^{98/95}$Mo = 2.48‰ on the basis of this study. When we assume Mo is completely conservative with *S* throughout the oxic ocean, the following equations would be valid:

$$[\mathrm{Mo}] = 2.89 \times S + 6 \quad (2)$$

$$\delta^{98/95}\mathrm{Mo} = -11.27 \times 1/[\mathrm{Mo}] + 2.59. \quad (3)$$

In our data, *S* varies from 33.052 to 36.727, which should result in variations in [Mo] from 102 to 112 nmol/kg and of $\delta^{98/95}$Mo from 2.48 to 2.49‰. However, no significant correlations were observed between [Mo] and *S* or between $\delta^{98/95}$Mo and 1/[Mo]. There are two possible explanations. One explanation is due to insufficient precisions in our analytical methods for [Mo] and $\delta^{98/95}$Mo. Another possibility is that small and real deviations from conservative behavior actually exist for Mo. Non-conservative signatures have actually been observed for dissolved Mo concentrations in estuarine and coastal waters (Dellwig *et al*., 2007; Rahaman *et al*., 2010) and in the eastern tropical Pacific (Tuit and Ravizza, 2003). The non-conservative signatures also reported for $\delta^{98/95}$Mo in the low salinity zone of an estuary (Pearce *et al*., 2010a). Possible mechanisms for non-conservative behavior of dissolved Mo in oxic seawater are uptake by phytoplankton and cyanobacteria, remineralization from biogenic particles, adsorption to Mn–Fe (oxyhydr)oxides, and reductive release from Mn–Fe (oxyhydr)oxides. Improvement in analytical methods and further observations are necessary to address the issue.

Mass-dependent isotope fractionation of Mo in the modern ocean

The total average values of $\delta^{A/95}$Mo are a strong linear function of the atomic mass. The regression line is $\delta^{A/95}\mathrm{Mo} = 0.8220 \times m - 78.00$ ($R^2 = 0.999$, SE = 0.07). The values of $\delta^{97/95}$Mo are plotted against those of $\delta^{98/95}$Mo in Fig. 6. The slope of the regression line passing through the origin is 0.675 ($R^2 = 0.541$, SE = 0.00085, n = 169). It is theoretically expected that the slope (β) of the three isotope plot is given by the following equations: for equilibrium mass-dependent isotope fractionation,

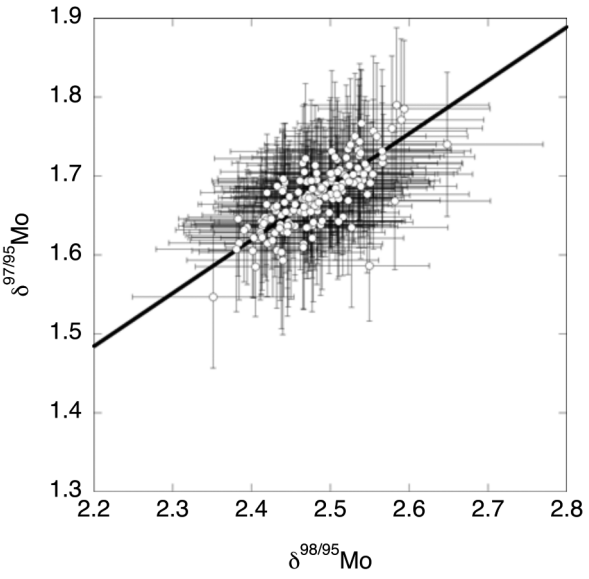

Fig. 6. $\delta^{97/95}$Mo vs. $\delta^{98/95}$Mo. The slope of the regression line passing through the origin is 0.675 (R^2 = 0.510). Error bars indicate ±2SE of the integrations in each analysis.

$$\beta = \frac{\left(\frac{1}{m_{95}} - \frac{1}{m_{97}}\right)}{\left(\frac{1}{m_{95}} - \frac{1}{m_{98}}\right)}$$

where m_i is the atomic mass of isotope *i*; for kinetic mass-dependent isotope fractionation,

$$\beta = \frac{\ln\left(\frac{m^*_{95}}{m^*_{97}}\right)}{\ln\left(\frac{m^*_{95}}{m^*_{98}}\right)}$$

where m^* represents the reduced atomic mass (Young *et al*., 2002). For $\delta^{97/95}$Mo vs. $\delta^{98/95}$Mo, the slope is estimated to be 0.674 for equilibrium fractionation and 0.675 for kinetic fractionation using a molecular moiety of Mo–O for calculating m^*. The observed slope is analytically identical to these values. Every plot between $\delta^{A/95}$Mo and $\delta^{98/95}$Mo gives similar results, though the correlations are never strong (R^2 = 0.175–0.735) because of narrow ranges in $\delta^{A/95}$Mo.

These results demonstrate for the first time, on the basis of a number of actual measurements, that the stable isotopes of dissolved Mo in the modern oxic ocean follow a mass-dependent fractionation law. It is most likely

Table 1. Mo isotppic composition in the modern oxic seawater

Ocean	Station or identity	Longitude	Latitude	Depths (m)	Molybdenum								
					Speciation	*n*	$\delta^{97/95}$Mo*	2SD	$\delta^{98/95}$Mo*	2SD	Concentration (nmol/kg)	2SD	References
Pacific													
		104.367°W	9.767°N	105		1	1.48						Barling *et al.* (2001)
	CTD-52			1600		1			2.4		115		Siebert *et al.* (2003)
						4			2.26	0.03			Archer and Vance (2008)
	Suruga Bay	138.32°E	34.85°N	687	Dissolved	13	1.67 (1.59)	0.09	2.47 (2.35)	0.08	103	3	Nakagawa *et al.* (2008)
	SAFe S1	140°W	30°N	0	Dissolved	3	1.62 (1.54)	0.07	2.37 (2.25)	0.11	106	4	Nakagawa *et al.* (2008)
	SAFe D2	140°W	30°N	1000	Dissolved	2	1.65 (1.57)	0.05	2.49 (2.37)	0.09	100	7	Nakagawa *et al.* (2008)
	K02	160.005°E	47.023°N	5–5133	Dissolved	20	1.69 (1.61)	0.07	2.48 (2.36)	0.09	107	7	This study
	KNOT	155.002°E	44.013°N	5–5264	Dissolved	23	1.67 (1.59)	0.06	2.48 (2.36)	0.08	105	4	This study
	35N	159.999°E	34.998°N	11–4500	Dissolved	20	1.68 (1.60)	0.07	2.48 (2.36)	0.09	106	4	This study
	St. 8	127.996°E	20.000°N	5–3925	Dissolved	19	1.65 (1.57)	0.06	2.44 (2.33)	0.09	108	7	This study
	St. 7	128.001°E	15.000°N	5–3927	Dissolved	21	1.66 (1.58)	0.05	2.47 (2.35)	0.08	106	5	This study
	SX18	169.999°W	39.998°S	5–4579	Dissolved	21	1.70 (1.62)	0.1	2.52 (2.40)	0.12	105	5	This study
Atlantic													
	IAPSO standard					1			2.3		115		Siebert *et al.* (2003)
	IAPSO standard								2.41	0.05	121		Pearce *et al.* (2009)
	CASS-4				Dissolved				2.23	0.09	92.1		Scheiderich *et al.* (2010)
	NASS-5			10	Dissolved	4	1.68 (1.60)	0.08	2.47 (2.35)	0.10	90	1	Nakagawa *et al.* (2008)
	ARI-1, coast					1			2.3		115		Siebert *et al.* (2003)
	Labrador Sea, FvB			2400		1			2.5		115		Siebert *et al.* (2003)
	Borgarfjörður estuary, C11	22.149°W	64.434°N	1	Dissolved				2.49	0.01	101		Pearce *et al.* (2010a)
	BATS	64.050°W	31.460°N	25–3935	Dissolved	13	1.67 (1.59)	0.07	2.48 (2.36)	0.07	105	6	This study
Southern													
	SX06	149.976°E	59.999°S	3–3161	Dissolved	18	1.69 (1.62)	0.07	2.51 (2.40)	0.08	106	3	This study
	SX09	174.155°E	65.146°S	4–3273	Dissolved	17	1.69 (1.61)	0.09	2.50 (2.38)	0.08	105	5	This study
Indian													
	CTD-24					1			2.3		115		Siebert *et al.* (2003)

**The values of Nakagawa et al. (2008) and this study were measured relative to a Johnson Matthey Mo standard solution. The vales in parentheses are corrected and expressed relative to the CPI Mo ICPMS standard that was used in Archer and Vance (2008).*

that this fractionation occurs in oxic sediments during adsorption to Mn oxides (Barling and Anbar, 2004; Wasylenki *et al*., 2008; Goldberg *et al*., 2009; Poulson Brucker *et al*., 2009). In addition, these results confirm the accuracy of our method and the precision of our results.

Synthesis of Mo isotopic data in the modern ocean

All the data for the isotopic composition of dissolved Mo in seawater from the literature and this study are summarized in Table 1. All the values of $\delta^{A/95}$Mo in Nakagawa *et al*. (2008) and this work are expressed relative to working standards that were prepared from the same lot of a Johnson Matthey Specpure Mo plasma standard solution. The resulting averages for each station converge in a narrow range: from 1.62 to 1.70 in $\delta^{97/95}$Mo, and from 2.37 to 2.50 in $\delta^{98/95}$Mo, whereas these values are relatively high compared to some literature values. We have compared the ^{98}Mo/^{95}Mo ratio between the standard used in this work and the CPI Mo ICPMS standard that was used in Archer and Vance (2008). Mo isotopic analysis revealed that $\delta^{98/95}$Mo of the standard in this study was –0.117 ± 0.009‰ (mean and 2SD of 5 different mixtures of the JM standard with double spike) relative to the CPI Mo ICPMS standard. The values in parentheses in Table 1 represent the $\delta^{A/95}$Mo of our seawater samples expressed relative to the CPI Mo ICPMS standard. The corrected $\delta^{A/95}$Mo show better agreement with some data, including that in Archer and Vance (2008). These results indicate that an internationally-certified Mo isotope standard is necessary for a sounder basis for the Mo isotopic composition in the ocean.

Lack of a common standard and reference material is a major problem in Mo isotope geochemistry (Hannah *et al*., 2007). Recently, Wen *et al*. (2010) compared the isotopic composition of Mo standard solutions and proposed the NIST 3134 Mo solution as a new candidate for a reference material to report Mo isotopic composition of natural samples. On the other hand, Siebert *et al*. (2003) proposed mean ocean water Mo (MOMO) as the reference for Mo isotopic composition. This proposal has not been widely adopted, probably because of the effort involved in preconcentration and separation of Mo from seawater. However, our data further confirm the homogeneous isotope composition of Mo in the ocean and recalls the possibility of using seawater as a reference material for Mo isotopic composition. The advantage of this reference material is that the ocean is one of the largest reservoir on the Earth and that the variations in isotope composition of Mo are as low as ~0.1‰ in δ-notation.

Conclusions

This study reports the full-depth distributions of every stable isotope of dissolved Mo in the modern oxic ocean for the first time. Each $\delta^{A/95}$Mo converges on a single global average, with 2SD less than 0.19‰. The average (relative to a Johnson Matthey Mo standard solution) and 2SD were as follows: $\delta^{92/95}$Mo = –2.54 ± 0.16‰, $\delta^{94/95}$Mo = –0.73 ± 0.19‰, $\delta^{96/95}$Mo = 0.85 ± 0.07‰, $\delta^{97/95}$Mo = 1.68 ± 0.08‰, $\delta^{98/95}$Mo = 2.48 ± 0.10‰, and $\delta^{100/95}$Mo = 4.07 ± 0.18‰. The modern oxic ocean is homogeneous in Mo isotope composition as well as in the Mo concentration, and any deviations are at a level less than the analytical uncertainty of the present technique. The first mass fractionation curve and three isotope plots for global seawater samples demonstrate the mass-dependent nature of Mo isotope fractionation in the modern oxic ocean. These results strongly support the possibility of seawater as an international reference material for Mo isotopic composition.

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